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INFLUENCE OF LASER ENERGY ON THE OPTICAL PROPERTIES OF Ag_2S ITO THIN FILMS PREPARED BY THE PLD TECHNIQUE

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Nanocrystalline silver sulfide (Ag_2S) thin films were prepared by the pulse laser deposition technique (PLD) on the indium-tin oxide (ITO) substrate at room temperature. In the PLD technique, an Nd : YAG laser with a wavelength of 1064 nm at different laser energies from 400 to 900 mJ is used with an increment of 100 mJ in each step with 200 pulses for each sample. The optical properties such as the refraction index n, absorption coefficient α, and extinction coefficient k are examined using the transmission and absorbance measurements on a UV-Vis-NIR spectrophotometer in the wavelength range (200–1100) nm. The average extinction coefficient is found between 0.076–0.163, while the average refractive index is between 2.214–2.528. The energy band gap decreases from 2.39 to 1.9 eV with increasing the laser energy.

K e y w o r d s: Ag_2S thin films, PLD technique, UV-Vis-NIR spectrophotometer, optical properties.

1. Introduction

Silver sulfide (Ag_2S) is a chemical compound found in nature in a black powder and also in the form of argentite metal [1]. Ag_2S belongs to the most important group of semiconductor compounds called chalcogenides. In recent years, metal chalcogenide semiconductor thin films have received a great attention to the large variety of different properties and the possibility of controlling and taking advantage of these properties [2]. The Ag_2S thin films are of great importance in industrial applications and due to their distinctive optoelectronic properties. They have been comprehensively investigated because of their use in broad areas, especially in devices due to their optical properties and in the electronic circuits. Therefore, there are many applications of thin films such as, capacitors, filters, electrical switches, IR detectors, solar cells, and magnetic field sensors, [3] *etc.*

Several techniques and methods to prepare Ag_2S thin films are available: the thermal evaporation, spray pyrolysis deposition (SPD), chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), and ion implantation techniques, [4] *etc.* The pulse laser deposition technique is considered as one of the most successful methods due to its high controllability, high quality, and relatively modest costs [5]. But Ag_2S thin films were not prepared previously by the PLD technique. Through this research, the success of the preparation of Ag_2S films was proven empirically in this method, and one of the most important factors studied is the influence of laser energy changes on the optical characteristic of the prepared nanoparticles.

2. Experimental

The deposition target was prepared from a pure Ag_2S powder, where the few amount of an Ag_2S powder was shaped as a squeezed disk 2.5 cm in diameter and 0.4 cm in thickness using a hydraulic compressor at a pressure of 10 tons. The pulse laser deposition technique was utilized to prepare the Ag_2S thin films in one step straight to the Indium Tin Oxide (ITO) substrate that is positioned above the target inside a vacuum chamber of the PLD system. The deposition was completed with a background pressure of 2×10^{-3} mbar. The Ag_2S target was radiated with a

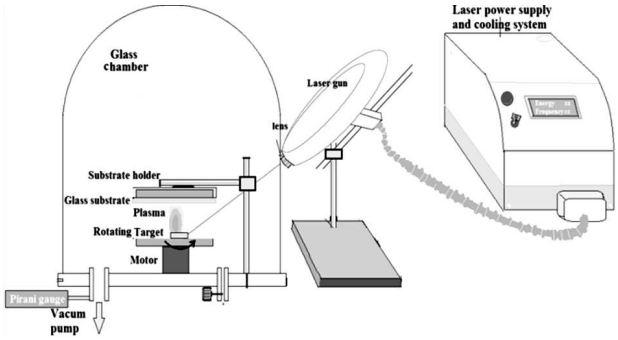


Fig. 1. Schematic diagram for the PLD system

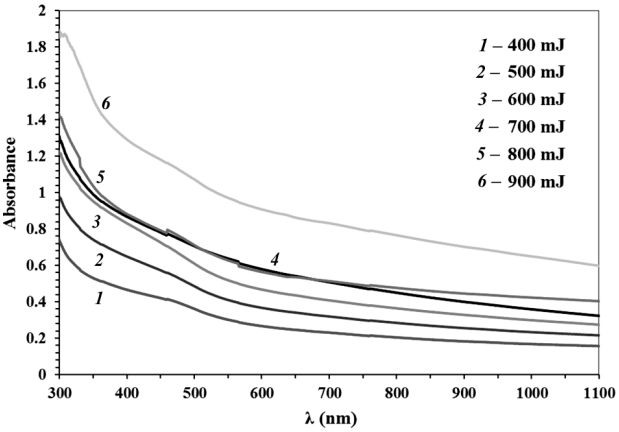


Fig. 2. Absorption spectra of Ag_2S thin films at different energies

Table 1. **Properties of Nd : YAG laser**

Energies (mJ/pulse)	Frequency (Hz)	Wavelength (nm)	Pulse period (nm)	Pulse diameter (mm)
400 500 600 700 800–900	6	1064	10	2.2

1064-nm Q-switched Nd : YAG laser (model HF-301, Huafei technology, China) with various laser energies for the constant number of pulses (200 pulse). The laser properties and factors considered in this experimental work are listed in Table 1. Lens with a focal length of 120 mm has been used to send the laser ray directly and accurately on the target. Figure 1 shows a schematic diagram for the PLD system.

3. Measuring Techniques

3.1. Thickness measurement

The optical interferometer technique was utilized to calculate the film thickness. This technique depends on the interference that occurs for light rays which are reflected from the film surface and the substrate base. A He–Ne laser has been utilized in this measurement process with a wavelength of 632.8 nm. The thickness is calculated according to the following equation [6]:

$$t = \frac{\Delta S}{S} X \frac{\lambda}{2}, \tag{1}$$

where S is the width of fringes, and ΔS is a shifting that happens with fringes.

3.2. Optical measurement

A double-beam UV-Vis-NIR spectrophotometer has been applied to study the absorptance and transmittance of Ag_2S thin films prepared under various conditions. The spectral range is estimated to be between (190–1100) nm. The background liquidation was considered for every scan. The measurement of transmittance and reflectance have been utilized in order to examined the absorption coefficient of films at various wavelengths. By using this measurement, the band gap energy has been calculated for prepared films.

4. Results and Discussion

Fig. 2 shows the absorption spectrum as a function of the wavelength in the wavelength UV-Vis-NIR range of pure Ag_2S thin films deposited at room temperature on the ITO substrates with different laser energies. It can be seen from this figure that the maximum absorption comes out at 300 nm. The absorptance of films increases with the laser energy from 400 to 900 mJ. This can be due to that more atoms are removed from the target surface, which leads to an increase in the thickness of thin films and causes a high absorption.

The absorption coefficient can be determined according to the following equation [7]:

$$\alpha = 2.303 \quad \mathrm{A/t}, \tag{2}$$

where t is the film thickness, and A is the absorbancy of a thin film.

The changes of the absorption coefficient α as a function of the wavelength for Ag_2S thin films for

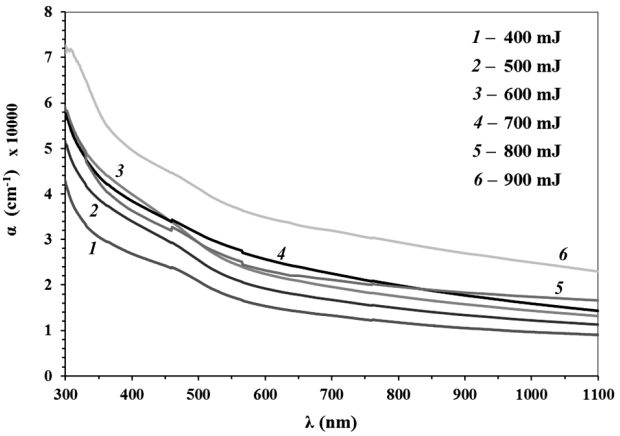


Fig. 3. Change of the absorption coefficient α of Ag_2S films with the wavelength for various laser energies

various laser energies from 400 to 900 mJ are shown in Fig. 3. The absorption coefficient α was calculated from the region of high absorption. It can be seen from this figure that the absorption coefficient increases with the laser energy due to increasing the film thickness.

The band gap energy of Ag_2S thin films was estimated graphically by using the Taucs relation for a direct transition, as shown in the relation 3 [8]:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^r, \tag{3}$$

where α is the absorption coefficient, h is Planck's constant, υ is the frequency, $h\upsilon$ represents the photon energy of the incident light, A is a constant, E_g is the band gap energy, and r is the exponential coefficient depending on the nature of the transition.

Figure 4 shows the relationship between the quantity $\alpha h\upsilon^2$ and how it changes with the photon energy($h\upsilon$. In order to calculate the band gap energy, the intersection of the estimated linear section of the curve with the photon energy axis at $(\alpha h\upsilon)^r = 0$ has been obtained, as shown in Fig. 4. This figure shows that the direct band hole of the film shifts toward lower energies. This means that the band gap energy is influenced by the laser energy, so that it decreases, as the laser energy increases. These results are listed in Table 2.

The extinction coefficient k can be determined from the equation given in the form [9]:

$$k = \frac{\alpha\lambda}{4\pi}, \tag{4}$$

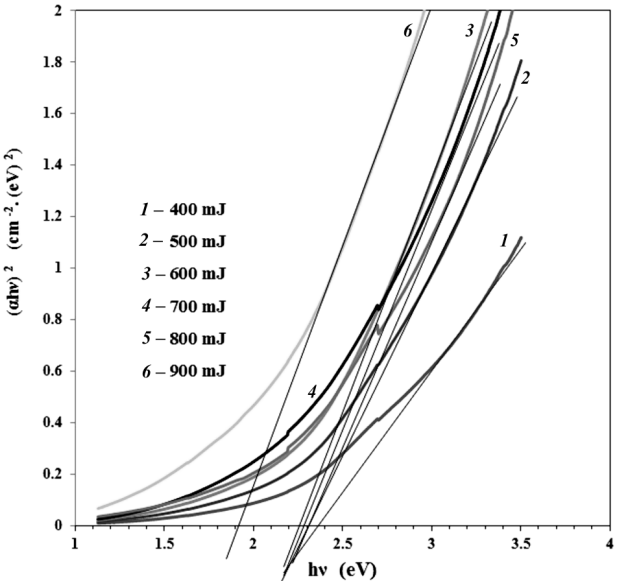


Fig. 4. $(\alpha h\upsilon)^2$ variation with the photon energy for Ag_2S films at different laser energies

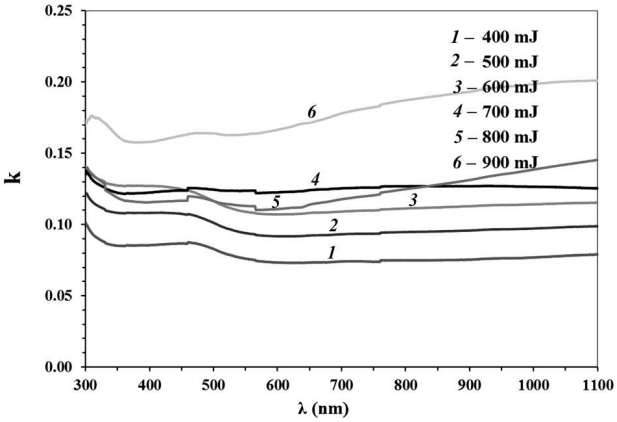


Fig. 5. Variation of the extinction coefficient k with the wavelength for Ag_2S thin films at various laser energies

Table 2. **Optical properties of Ag_2S thin films under the action of the 550-nm solar radiation**

Energies, mJ	T%	α, cm^{-1}	K	n	ε_r	ε_i	E_g, eV
400	70.65	17370	0.076	2.214	4.895	0.337	2.39
500	62.35	21470	0.094	2.413	5.812	0.454	2.31
600	55.03	24887	0.109	2.548	6.480	0.555	2.30
700	47.97	28253	0.124	2.628	6.890	0.650	2.26
800	48.53	25822	0.113	2.624	6.871	0.593	2.25
900	32.67	37286	0.163	2.528	6.363	0.825	1.90

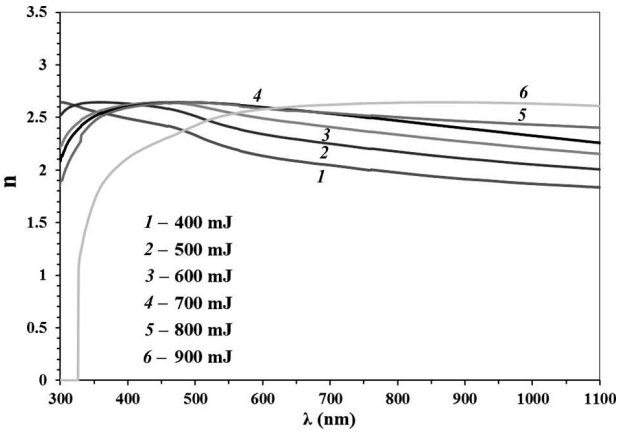
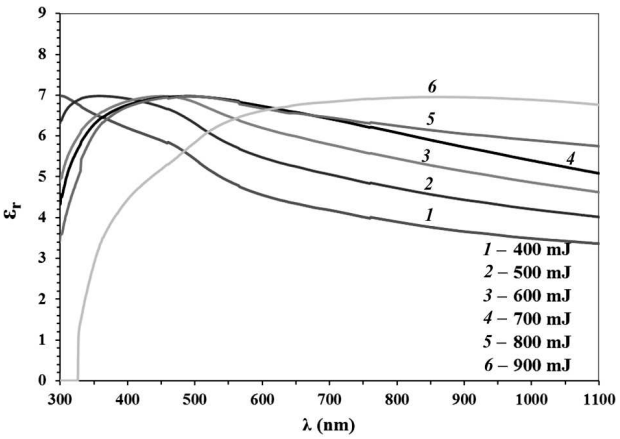
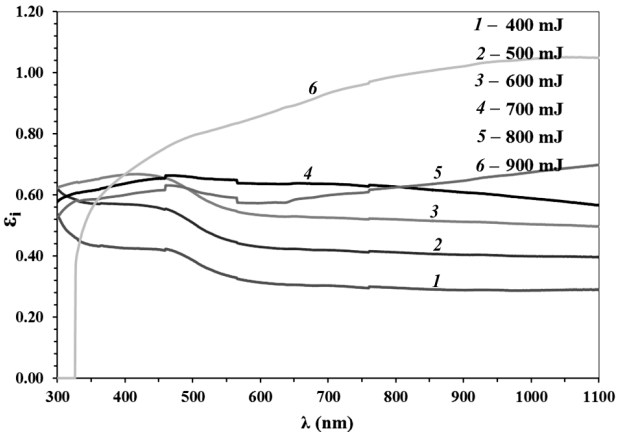


Fig. 6. Dependence of the refractive index on the wavelength for Ag_2S films at different laser energies



a



b

Fig. 7. Variation of the real (*a*) and the imaginary (*b*) dielectric constants with the wavelength for Ag_2S films at different laser energies

where α is the absorption coefficient, and λ is the wavelength.

Figure 5 shows the extinction coefficient k as a function of the wavelength for Ag_2S thin films with various laser energies from 400 to 900 mJ. It can be observed that the extinction coefficient increases with the laser energy.

Figure 6 shows the refractive index and how it changes with the wavelength for Ag_2S thin films at different laser energies. This figure indicates that the refractive index increases slightly with the laser energy for all prepared samples. This can be explained on the basis of the improvement in the crystallization of Ag_2S films with increasing the laser energy.

The real and imaginary parts of the dielectric constant ε are related to the extinction coefficient k and the refractive index n by the following relations [10]:

$$\varepsilon_r = n^2 - k^2, \tag{5}$$

$$\varepsilon_i = 2nk, \tag{6}$$

where ε_r is the real part, and ε_i is the imaginary part.

Figures 7, *a* and *b* show the difference of the real and imaginary parts of the dielectric constant versus the wavelength for Ag_2S with different laser energies.

5. Conclusion

In this paper, nanocrystalline Ag_2S thin films have successfully been prepared on the ITO substrates by using the Pulse Laser Deposition technique at room temperature. The optical properties are investigated at different laser energies. The results obtained on a UV-Vis-NIR spectrophotometer show that if the laser energy increases, the absorption coefficient of the films increases as well. The optical band gap for a film is influenced by the laser energy so that it decreases (2.39, 2.31, 2.3, 2.26, 2.25, and 1.9 eV), as the laser energy increases (400, 500, 600, 700, 800, and 900 mJ), respectively. These values of band gaps are required for solar absorber films in the solar cell fabrication.

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ЗАЛЕЖНІСТЬ ОПТИЧНИХ ВЛАСТИВОСТЕЙ ТОНКИХ Ag_2S ПЛІВОК НА ОКСИДІ ІНДІЮ-ОЛОВА, ВИГОТОВЛЕНИХ ОСАДЖЕННЯМ ЗА ДОПОМОГОЮ ЛАЗЕРНИХ ІМПУЛЬСІВ, ВІД ЕНЕРГІЇ ЛАЗЕРА

Р е з ю м е

Нанокристалічні тонкі плівки сульфіду срібла (Ag_2S) були виготовлені осадженням за допомогою лазерних імпульсів на оксиді індію-олова при кімнатній температурі. Використовувався Nd : YAG лазер з довжиною хвилі 1064 нм при різних енергіях (від 400 до 900 МДж) з приростом 100 МДж на кожному кроці. На один зразок припадало 200 імпульсів. Досліджено такі оптичні властивості, як показник заломлення n, коефіцієнт поглинання α і коефіцієнт екстинції k за допомогою вимірювання пропускання і поглинання на UV-Vis-NIR спектрофотометрі в інтервалі довжин хвиль 200–1100 нм. Середні величини коефіцієнта екстинції і показника заломлення рівні 0,076–0,163 і 2,214–2,528, відповідно. Ширина забороненої зони зменшується від 2,39 до 1,9 еВ при збільшенні енергії лазера у вказаному вище інтервалі.